Journal of Chromatography, 282 (1983) 579–587
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CHROMSYMP. 165

HIGH-PERFORMANCE SIZE-EXCLUSION CHROMATOGRAPHY OF POLYAMIDE 6

H. SCHORN, R. KOSFELD* and M. HESS
Universität —Gesamthochschule— Duisburg, FB 6 — Physikalische Chemie, Bismarckstrasse 90, 4100 Duisburg (F.R.G.)

SUMMARY

In order to evaluate the distribution function of the molar mass of Polyamide 6, size-exclusion chromatography on porous silica in hexafluoroisopropanol with added sodium trifluoroacetate was investigated. The experimental set-up consisted of a slightly modified liquid chromatographic system, equipped with a highly sensitive refractive-index detector, a laser low-angle light-scattering photometer, a programmable autosampler, and a computing integrator.

This equipment is capable of delivering such important data of the system studies as: the specific refractive index increment at the wavelength of the incident beam of the photometer, the second virial coefficient, A_2, of the polymer solvent system, and the distribution function of the polymer with average $\langle M_w \rangle$, $\langle M_n \rangle$, and $\langle M_z \rangle$ of the molar masses. The influence of sodium trifluoroacetate concentration on the chromatographic behaviour is discussed.

INTRODUCTION

Owing to their solubility and solution behaviour the polyamides cannot be chromatographically analysed as easily as, *e.g.*, polystyrene. The usual solvents and/or temperatures are unsuitable and degradation of the polymer chains may occur[1]. Polyelectrolyte effects[2,3] may also occur and lead to misinterpretation of the chromatograms.

An alternative method is derivatisation of the polyamide. This was carried out by Jacobi *et al.*[4], who prepared the N-trifluoroacetylated polyamide. Ordinary solvents, such as dichloromethane, chloroform, tetrahydrofuran, dioxane, acetone and N,N-dimethylformamide are then applicable. Nevertheless, the product had undergone chemical reactions, and the chromatographically analysed sample was not the original one. Jacobi *et al.* did not find any disadvantages in this procedure, but, we observed insoluble residues and incomplete reactions.

Drott[5] found hexafluoroisopropanol (HFIP) to be a suitable solvent at room temperature, but it had the disadvantages that the polymer in solution shows polyelectrolyte effects[2,3] and that the solvent is expensive. The first shortcoming can be avoided by addition of sodium trifluoroacetate (NaTFA), the second by recycling the solvent.

0021-9673/83/$03.00

The introduction of laser low-angle light-scattering (LLALS) devices[6] as detectors[7,8] in polymer liquid chromatography gave rise to much more sophisticated interpretation of the chromatographic elution curves than the refractive index (RI) or UV detector alone. Calibration with narrow-distribution standards are no longer necessary if the dependence of the specific RI increment and second virial coefficient on molar mass is known[8,9].

THEORY

In polymer characterisation, number average, weight average, and z-average of the molar mass play important roles[10].

$$\langle M_n \rangle \equiv \frac{\sum w_i}{\sum \frac{w_i}{M_i}} \tag{1}$$

$$\langle M_w \rangle \equiv \frac{\sum w_i M_i}{\sum w_i} \tag{2}$$

$$\langle M_z \rangle \equiv \frac{\sum w_i M_i^2}{\sum w_i M_i} \tag{3}$$

where w_i = mass of species i and M_i = molar mass of species i.

Usually, the averages 1–3 are not informative enough for the characterisation of a distribution. The distribution function itself reveals much more information

$$w(M) = \frac{\mathrm{d}J_w(M)}{\mathrm{d}M} \tag{4}$$

where $J_w(M)$ is the cumulative (integral) molar mass distribution function. The distribution function shows the ratio of mass between M and $M + \mathrm{d}M$.

By combining size-exclusion chromatography for separation, light-scattering photometry at low scattering angles for measurement of Rayleigh ratio $\Delta R_{\theta\rangle i}$, and RI detection for determination of the corresponding concentration c_i with adequate data processing, it is possible to evaluate the distribution function, together with the averages 1–3, quickly and easily without calibration in an absolute procedure.

The differences in elution volume, ΔV_{el}, which $\Delta R_{\theta\rangle i}$ and c_i are so narrow that for these values $M_i = M_w = M_n$ is valid. Thus, the relationship between the molar mass M_i at a distinct time of the chromatogram or with a definite elution volume V_{el} and the Rayleigh ratio is given by[9]

$$M_i = \frac{1}{\frac{k \cdot c_i}{\Delta R_{\theta,i}} - 2A_{2,i} \cdot c_i} \tag{5}$$

The symbols used have the following meaning:

$\Delta R_{\theta,i}$ is the difference of the Rayleigh ratios between sample and pure solvent at scattering angle θ, corresponding to the concentration c_i. The Rayleigh ratio is defined as the quotient of intensity of scattered light to that of the light at $\theta = 0$.

M_i is the molar mass at the elution volume $V_{el,i}$, corresponding to $\Delta R_{\theta,i}$ and c_i.

c_i is the mass concentration at elution volume $V_{el,i}$.

$k = \dfrac{2\pi^2 n^2}{\lambda^4 N_L}\left(\dfrac{dn}{dc}\right)^2 (1+\cos^2\theta)$.

n is the refractive index at the incident wavelength.

λ is the wavelength of the incident beam.

N_L is Avogadro's constant.

$\dfrac{dn}{dc}$ is the specific refractive index increment at incident wavelength.

θ is the scattering angle.

The scattering angle, θ, is so small (6° to 7°) that no extrapolation $\theta = 0$ is necessary. The Rayleigh ratio is calculated from the attenuated intensities of the scattered light, $\Delta G_{\theta,i}$, at the angle θ and from the corresponding value G_0 of the unscattered beam by means of the operating parameters D,σ', and l' of the photometer and via eqn. 6

$$\Delta R_{\theta,i} = \frac{\Delta G_{\theta,i}}{G_0}\frac{D}{\sigma' l'} \tag{6}$$

where $\Delta G_{\theta,i} = G_{\theta,i} - G_{\theta,0}$ (7)

and $G_{\theta,0}$ is the attenuated scattering intensity of the pure solvent; c_i is calculated from the RI. Both chromatographic elution curves, which are due to the signals of LLALS and RI, are digitalised and data-processed.

As the LLALS response is very sensitive to particles larger than the polymer molecules (M_i scattering) spikes may occur during chromatographic analysis which have to be cut from the elution curve before calculation of the distribution to avoid errors. After the spikes are cancelled, the second virial coefficient A_2 is calculated by using eqn. 5 and measuring $\Delta R_{\theta,i}$ and c_i at the same elution volume, $V_{el,i}$, at several concentrations. The evaluated $A_2(M_i)$ is then used to estimate the corresponding M_i from eqn. 5. When this procedure is carried out at different elution volumes, it yields the dependence of A_2 on the molar mass of the polymer. The parameters of the function may be found by fitting the calculated values to the general estimate[10]

$$A_{2,i} = k \cdot M_i^{-\alpha} \tag{8}$$

k, α being constant factors.

EXPERIMENTAL

The experimental set-up is shown in Fig. 1. The three-port valve enables quick measurement of the specific RI increment dn/dc of the system with a highly sensitive

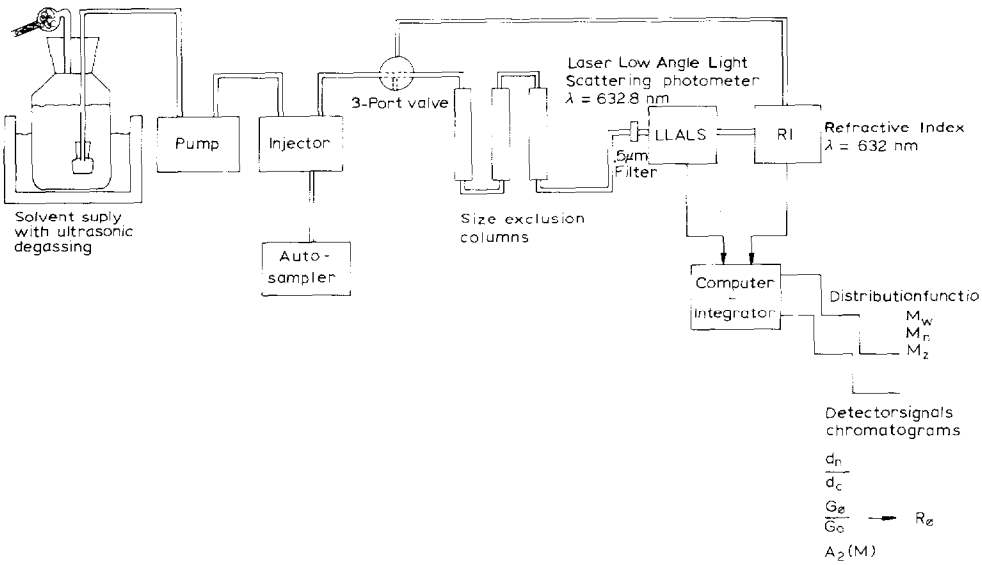

Fig. 1. Experimental set-up.

RI detector, based on the interferometric principle. The dependence on molar mass can be calculated by using polymer samples with narrow distribution of molar masses. If the dependence of dn/dc on molar mass is negligible, the average value can be used.

The equipment used consisted of: a, Waters 6000A pump; a Waters programmable automatic injection system WISP; Knauer columns: LiChrosphere Si-100, Si-500, and Si-1000; exclusion range $\simeq 10^3$ to $2 \cdot 10^6$ gmol^{-1}; Chromatix KMX-6 $\lambda = 632$ nm LLALS photometer; Optilab Multiref 90B interference refractometer $\lambda = 632$ nm. Chromatographic parameters: T, 25°C; flow-rate, 0.5 ml min^{-1}; pressure drop, 1500 p.s.i.; injected volume, 0.1 ml; injected concentrations $0.2 \cdot 10^{-2}$ to 10^{-2} g ml^{-1}.

Solvents were degassed by ultrasonic treatment. The solvent system consisted of freshly distilled HFIP (Merck, Darmstadt, purity greater than 99%) containing different amounts of NaTFA to suppress polyelectrolyte effects[3,5–11]. NaTFA was prepared in the following manner: trifluoroacetic acid anhydride was hydrolysed to the corresponding acid, which was subsequently exactly neutralised with Na_2CO_3 and evaporated.

The samples were prepared as follows: NaTFA was dissolved in HFIP in the appropriate concentration under strict exclusion of humidity and under N_2 protection; the necessary amount of dry Polyamide 6 (PA-6) was added and the solution was allowed to equilibrate overnight with slight stirring. No change of solution composition was observed for weeks under these conditions.

The programmable injection system greatly facilitates recording several concentration-dependent chromatograms. The scheme of data acquisition is shown in Fig. 2. The detector outputs were processed by a Spectra-Physics SP-4200 computing integrator.

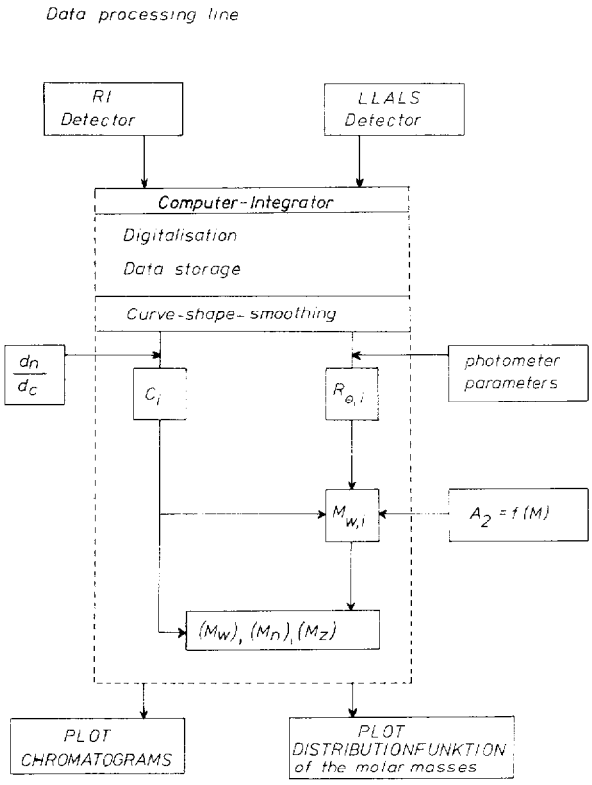

Fig. 2. Diagram of the data processing line.

RESULTS

Fig. 3 shows the effect of NaTFA on chromatographic behaviour. Down to a concentration of 0.0005 *M* NaTFA in HFIP polyelectrolyte effects of polyamide and adsorption effects are suppressed, as can be deduced from the absence of additional peaks in the chromatogram, especially from the light-scattering data. Separation must take place within the dead-volume of the column, otherwise the assumptions are not valid for correct calculation. In Fig. 4 the calculated differential distribution function of the molar mass is plotted. The averages 1–3 are marked. The second virial coeffiicient is found to be zero if polyelectrolyte effects are suppressed, as may be expected from theory[2] $dn/dc_{\lambda=632\ nm}$ was determined by using the chromatographic system via the bypass.

$$(dn/dc)_{\lambda=632\ nm}\ (\text{HFIP}/5 \cdot 10^{-4}\ M\ \text{NaTFA}) = 0.2375 \pm 0.025\ \text{ml g}^{-1}$$
$$n_{632\ nm}^{25°C} = 1.2754 \pm 0.0002$$

Fig. 5 documents the effect of spike-smoothing. Solvents without additional salt show a much better, *i.e.* spike-free chromatogram. The materials producing the spikes in the light-scattering experiment with salt-containing solutes may be produced in the

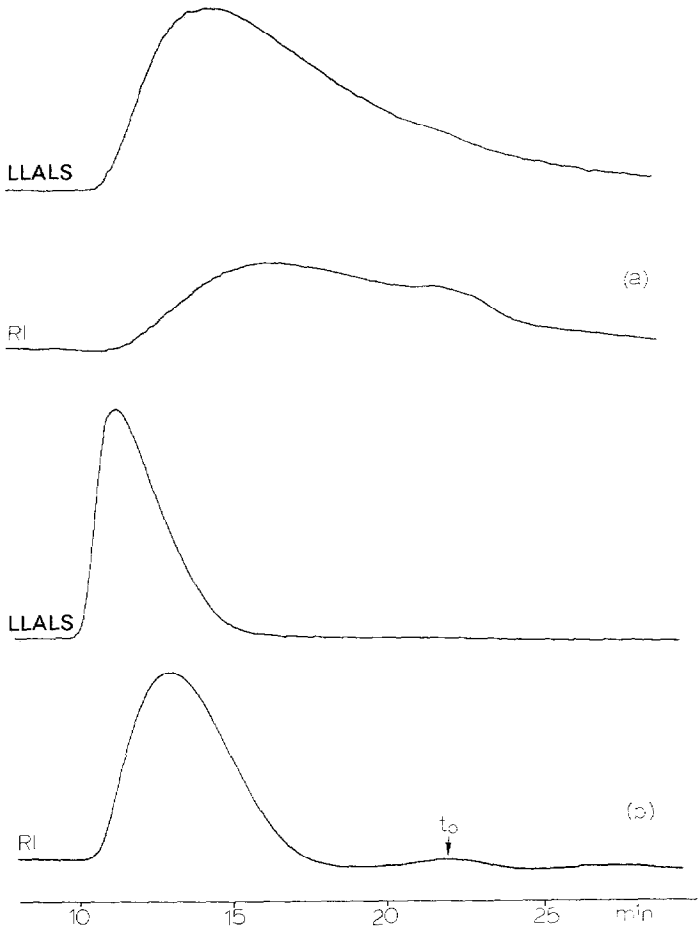

Fig. 3. Two chromatograms of the same PA-6 at two different compositions. (a) Pure HFIP as solvent; (b) HFIP containing 0.0005 *M* NaTFA. The polyelectrolyte effect is suppressed. The low-molecular peaks due to the RI signal have no corresponding *R*. They can therefore be disregarded when calculating the distribution.

chromatographic tubes as may be deduced from deposits occasionally observed on cuvette surfaces. Fig. 5 clearly shows that there is no falsification of signals, either due to digitisation or to our smoothing programme.

DISCUSSION

As shown in Fig. 3, the polyelectrolyte effect[2,5,11] of PA-6 in HFIP containing a minimum 0.0005 *M* NaTFA is suppressed and no adsorption on LiChrosphere Si-columns is observed, as has been reported for benzyl alcohol as high-temperature solvent[1]. Without NaTFA, formation of hydrogen bonds is favoured. These bonds may be formed with neighbouring PA-6 chains to form aggregates or they may be effective in adsorption processes.

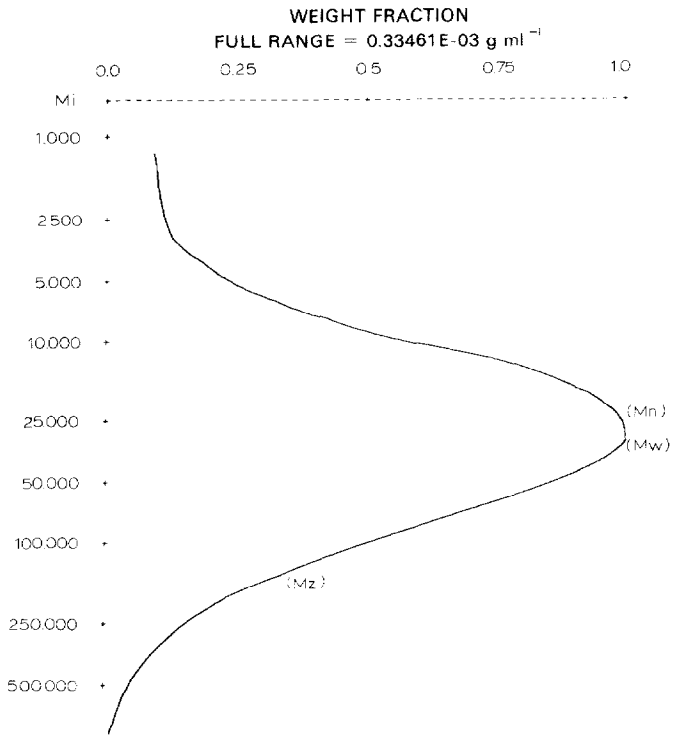

Fig. 4. Differential molar mass distribution of a PA-6 sample with totally suppressed polyelectrolyte effect. If polyelectrolyte effects occur, odd distribution functions occur due to imperfect separation.

LLALS gives detailed information about the behaviour of the polymer. This detector shows some advantages in the analysis of systems where narrowly distributed standards are rare, and polystyrene is not suitable as a reference material. Moreover, the detector gives much more information about the chromatographic separation process, as it is directly sensitive to the size of the scattering molecule and, thus, M_w. If the material is retained by an adsorption mechanism and so takes a larger elution volume than dead-volume, this will clearly be visible with LLALS. The RI or UV detector only reports the concentration of whatever flows through it. Now polymeric material can clearly be distinguished from solvent impurities or density inhomogenities due to injection of the sample by monitoring the light-scattering signal. As the calculation of M_i by LLALS is an absolute method, generally no standards are needed, and the distribution function may be calculated on-line. The resulting shape of the distribution also gives hints concerning the chromatographic process.

The calculated distribution function of the analysed PA-6 (Fig. 3) shows a material of common quality with the expected value of *ca.* 2 for $\langle M_w \rangle / \langle M_n \rangle$, as it should in the Schulz–Flory distribution[1,12,13].

The average viscosity molar mass $\langle M_\eta \rangle$ is in the region calculated from viscosity measurements in different solvents. $\langle M_n \rangle$ agrees well with the end-group titration of NH_2 with HCl.

In the experimental set-up, emphasis must be placed on the need for a proper

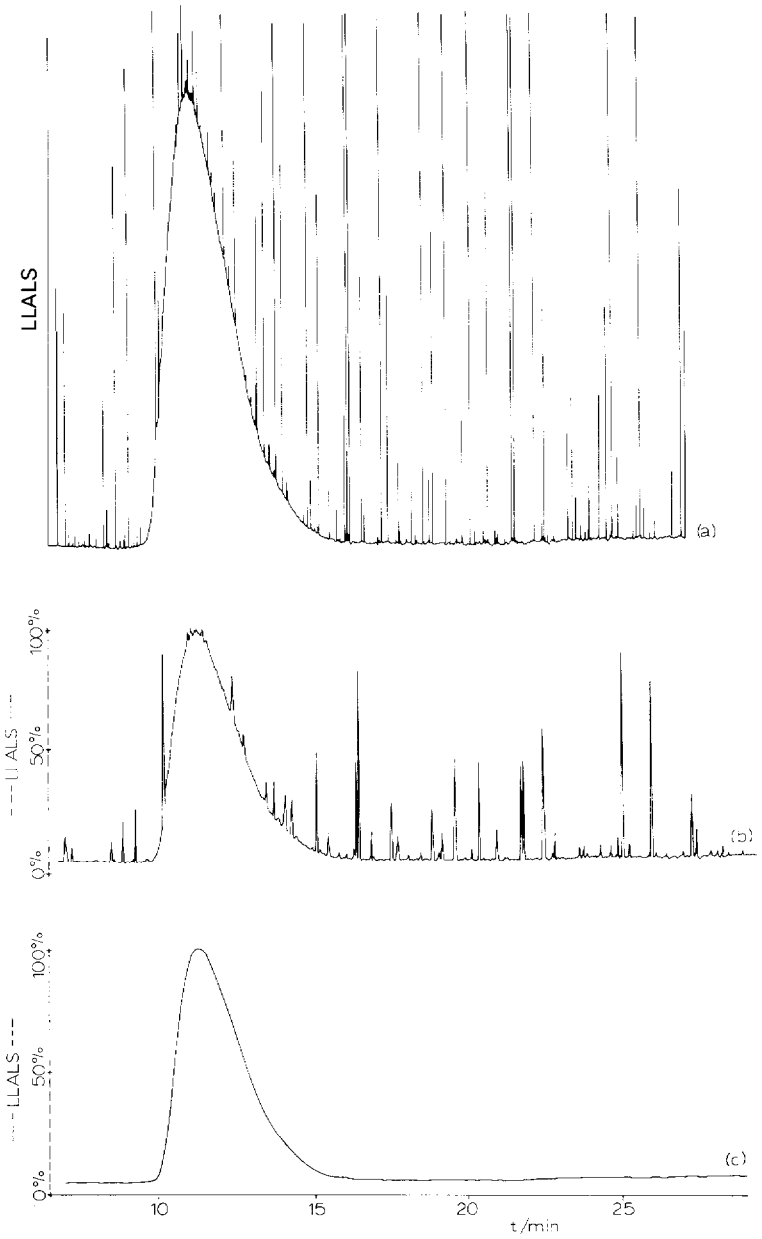

Fig. 5. Effect of data processing on outer shape of elution curves. (a) Analog output of a conventional recorder. The light-scattering signal is superposed by several spikes. (b) Same elution curve after analog–digital processing. (c) Same elution curve after cancelling of spikes.

evaluation of the different delay times of the sequential detectors. Their signals must be exactly synchronised. Other causes of error are the baseline correction and the determination of integration limits. In many cases we have found that the limit of

0.2% deviation from baseline (peak maximum being 100% deviation) of the LLALS is sufficient for integration limits. Miscalculation does not lead to a wrong value for $\langle M_w \rangle$ but to wrong values for $\langle M_n \rangle$ and $\langle M_z \rangle$.

CONCLUSION

HFIP is suitable as a mobile phase in liquid size-exclusion chromatography of PA-6 on unmodified silica columns, if a minimum concentration of 0.0005 *M* NaTFA is used. Strict exclusion of water is necessary to avoid the formation of corrosive products. An appropriate cancelling of spikes in the LLALS signal can be achieved by water exclusion, filtration, and sophisticated data processing.

ACKNOWLEDGEMENT

We thank Professor W. Borchard, Universität —Gesamthochschule— Duisburg, FB 6 — Angewandte Physikalische Chemie for helpful discussion.

REFERENCES

1 G. Pastuska and U. Just, *Angew. Makromol. Chem.*, 81 (1979) 11.
2 H. J. Schönert, *Kolloid. Z.*, 176 (1961) 14.
3 G. Scatchard, *J. Amer. Chem. Soc.*, 68 (1946) 2315.
4 E. Jacobi, H. Schuttenberg and R. C. Schultz, *Macromol. Chem. Rapid Commun.*, 1 (1980) 397.
5 E. E. Drott, in J. Cazes (Editor), *Liquid Chromatography of Polymers and Related Materials*, Chromatographic Sciences Series Vol. 8, Dekker New York, Basel, 1977, p. 41.
6 U. Kröpf, *Laser in der Chemie*, Salle & Sauerländer, Bielefeld, 1978.
7 A. C. Ouano and W. Kayl, *J. Polym. Sci., Polym. Chem. Ed.*, 12 (1974) 1151.
8 A. C. Oauno, *J. Chromatogr.*, 118 (1976) 303.
9 M. B. Huglin (Editors), *Light Scattering from Polymer Solutions*, Academic Press, New York, 1982.
10 J. P. Flory, *Princciples of Polymer Chemistry*, Cornell University Press, London, 1953.
11 C. Y. Cha, *J. Polym. Sci., Part B*, 7 (1969) 343.
12 C. Y. Schulz, *Z. Phys. Chem.*, 182 (1938) 127.
13 J. P. Flory, *J. Amer. Chem. Soc.*, 58 (1936) 1877.